6-1987

Synthesis of 3, 6-dimethyl-9, 10-bis (trimethylsilyl) diimine: structural modification of an electrically conductive organic solid

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Synthesis of 3,6-dimethyl-9,10-bis(trimethylsilyl)diimine: Structural Modification of an Electrically Conductive Organic Solid

By

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Submitted in partial fulfillment of the requirements for Honors in the Department of Chemistry

Union College

June, 1987

ABSTRACT

MORPHET, CYNTHIA Synthesis of 3,6-dimethyl-9,10-bis(trimethylsilyl)-diimine: Structural Modification of an Electrically Conductive Organic Solid

The current, intense interest in non-classical electrical conductivity and superconductivity has stimulated an equally intense effort to synthesize new materials which exhibit enhanced electrical conductivities. This thesis reports such an effort.

Previous work had resulted in the formation of planar aromatic compounds capable of acting as "synthetic metals", i.e.: of conducting an electrical charge. These efforts had focused on compounds utilizing heteroatoms from Group VIA.

Efforts to synthesize analogous compounds utilizing heteroatoms from Group VA had been partially sucessful, but were hampered by solubility considerations. This research focuses on the synthetic procedure developed to produce an anolog of one of these compounds with enhanced solubility properties.

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Introduction:

Electrical conductivity is such an inherent part of everyday life that it is easy to assume that there is nothing left to be learned about the subject. Yet, new ways to produce, utilize, and, especially conduct electricity still await discovery.

In order to be capable of conducting electricity, a substance must possess both charge carriers and a continuous pathway for charge carrier movement. Traditionally, the ability to conduct electricity has been associated with metals. In metals, the metal nuclei and core electrons are arranged in a crystal lattice. However, the valence electrons, which serve as charge carriers, are only loosely bound to the metal nuclei. The effective result is to form a "sea" of electrons that is free to move throughout the metal.

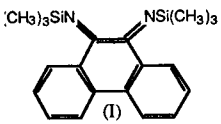
Certain nonmetal compounds also display the ability to conduct electricity. In a molecule, each atom contributes atomic orbitals to produce molecular orbitals that extend throughout the molecule. When a number of molecules are assembled together to form a solid, the energy differences between intermolecular mo's become indistinguishable. The effective result is to form a continuous band of molecular orbitals that extends throughout the entire structure. The spacing and filling of these bands determine the electrical properties of the material. Partially filled bands, or completely filled bands that overlap with empty bands yield a material capable of conducting electricity. Completely filled bands

separated from empty bands by a small energy gap yield semiconductors, while separation by a large energy gap yields insulating materials.

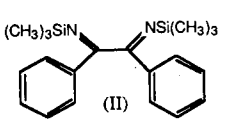
Most organic materials are not capable of conducting electricity. However, some organic compounds, particularly those with extensive conjugation, have the potential to become conductors. If molecules of these compounds are arranged in close spatial proximity in such a way as to produce the parallel overlap of their pi systems, a continuous pathway for charge carrier movement is formed, and charge carriers are formed through incomplete charge transfer between the pi systems. These effects are most pronounced in planar donor molecules that have been arranged into linear stacks, consisting either of donor molecules doped with acceptor molecules, or segregated stacks of donor and acceptor molecules.

Other research efforts have resulted in the synthesis of donor and acceptor molecules, such as Tetrathiofulvalene (TTF) and Tetracyanoquinodimethane (TCNQ), utilizing heteroatoms from Group VIA.

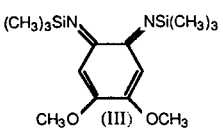
The purpose of this research was to synthesize donor molecules utilizing heteroatoms from Group VA. Prior research had resulted in the synthesis of three such donor molecule precursors:



(I)



(II)



(III)

(I) has a high potential for planarity, and thus for arrangement into linear stacks, but solubility considerations limit its usefulness. The main thrust of this research is to synthesize a ring substituted dimethyl analog of (I) in an effort to improve its solubility in non-aromatic solvents, resulting in more efficient separation, purification, and characterization of subsequent donor molecules.

Experimental:

Part One: The Preparation of di-p-tolylchloroethane :[1]

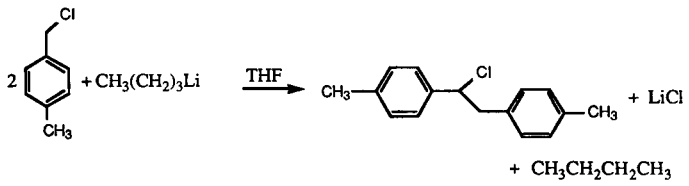
A three-necked, 500 ml, round-bottomed flask was equipped with a stopper, an overhead stirrer, and a 125 ml vented addition funnel with a septum and a nitrogen inlet. A vent needle was inserted into the septum, and the apparatus was purged with nitrogen and flame dried with a bunsen burner to eliminate water. A slow, continuous nitrogen flush was established through the apparatus. A volume of 30 ml (0.225 mol) of α-chloro-para-xylene was measured into a graduated cylinder in the hood and added rapidly to the reaction flask through a funnel in the stoppered neck. A volume of 300 ml of tetrahydrofuran was added into the reaction flask through a cannula through the addition funnel. The stirring apparatus was turned on and the solution was cooled in an ethanol-liquid nitrogen slush bath in a dewar to -100°C. A volume of 70.3 ml (0.1125 mol) of n-butyllithium (1.6 N in hexanes) was added into the addition funnel through a cannula inserted through the septum. The n-butyllithium was dripped into the reaction flask at a rate slow enough to maintain the reaction mixture at -100°C. After all of the n-butyllithium was added to the reaction flask, the reaction mixture was allowed to gradually warm to ambient temperature with the dewar in place, and was stirred overnight.

The reaction was quenched by pouring the reaction mixture into an equal volume of ice water. The quenced mixture was poured into a 1000

ml separatory funnel, and the denser water layer was separated and discarded. The less dense organic layer was poured into an Erlenmeyer flask and dried over magnesium sulfate overnight. The organic layer was separated from the magnesium sulfate by gravity filtration, and the magnesium sulfate was washed twice with hexane to remove any remaining organic material.

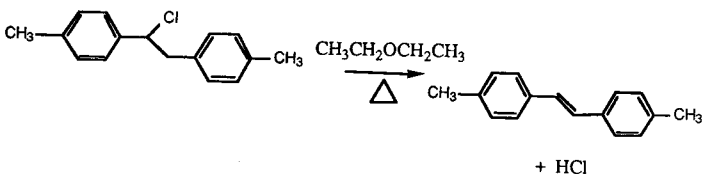
The organic layer was rotovapped to separate the product from the tetrahydrofuran and hexane. The oil obtained from rotovapping was cooled in the refrigerator to induce crystallization. The white solid obtained was vacuum filtered on a Buchner funnel and washed with cold hexane, and the filtrate was concentrated by rotovapping and recooled to obtain more solid.

The product was characterized by melting point. If the melting point was less than $30^{o}C$, the solid was dissolved in diethyl ether and recrystallized by cooling.



Part Two: The Preparation of 4,4'-dimethyl-trans-stilbene[1]

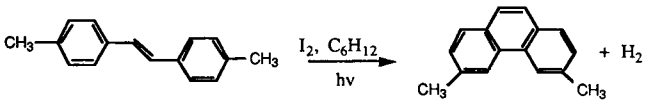
A three-necked, 500 ml, round-bottomed flask was equipped in the hood with a septum and nitrogen inlet, a condensor and bubbler, a thermometer, and a magnetic stirring bar. All of the di-p-tolylchloroethane (approximately 15 g.) was dissolved in a minimum volume of diethyl ether and transferred to the reaction flask through a funnel in the thermometer neck. A slow, continuous nitrogen flush was established through the apparatus, the magnetic stirrer was turned on, and the reaction mixture was gradually heated with a heating mantle. The reaction mixture was allowed to stir at 180°C overnight. The emitted vapor was tested for acidity with moist litmus paper. When the vapor no longer registered as acidic, the reaction mixture was allowed to cool gradually with the heating mantle in place. The product crystallized on the walls of the reaction flask above the level of the heating mantle. The white solid obtained was dissolved in hot absolute ethanol and cooled in the refrigerator to induce crystallization. The white crystals obtained were vacuum filtered on a Buchner funnel and washed with cold hexane, and the filtrate was concentrated by rotovapping and recooled to obtain more solid. The product was characterized by NMR spectroscopy.



+ HCl

Part Three: The Preparation of 3,6-dimethylphenanthrene[2]

A photolytic apparatus was assembled that consisted of a quartz immersion well, water jacket, and reaction vessel, a condensor, and a Hanovia mercury lamp. A mass of 0.52 g (0.0025 mol) of 4,4-dimethyl-trans-stilbene and 0.03-0.04 g of iodine were dissolved in 250 ml of hot cyclohexane. The resulting violet solution was poured into the photolysis apparatus's reaction vessel, a steady flow of water was established through the water jacket and condensor, and a steady flow of air was established through the solution. The mercury lamp was turned on, and the reaction mixture was photolyzed for two hours, or until the reaction mixture underwent a color change to orange and solid precipitated on the walls of the reaction vessel. The reaction mixture was rotovapped to dryness, and the orange solid obtained was dissolved in hot methanol and cooled in the refrigerator to induce crystallization. The orangish-gold crystals obtained were vacuum filtered on a Buchner funnel and washed with cold methanol. The filtrate was concentrated by rotovapping and recooled to obtain more solid. The product was characterized by NMR spectroscopy.

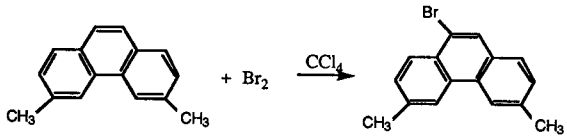


Part Four: The Preparation of 9-bromo-3,6-dimethylphenanthrene[3]

A mass of 4.75 g (0.02303 mol) of 3,6-dimethylphenanthrene was dissolved in a minimum volume of carbon tetrachloride in an Erlenmeyer flask and the solution was cooled to $0^{o}C$ in an ice water bath. A volume of 0.6 ml (0.01151 mol) of bromine was added to the solution through a syringe, and the dark reddish-brown reaction mixture was allowed to warm to ambient temperature and stand for two hours in the hood. The reaction mixture was rotovapped and the resulting dark brown liquid was heated over a steam bath for 30 minutes.

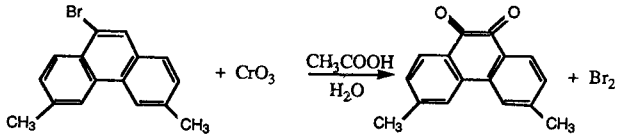
Silica gel was prepared for column chromatography as follows: Silica gel was slurried in twice its volume of deionized water, and the slurry was allowed to stand at ambient temperature for one hour. The slurry was then vacuum filtered on a Buchner funnel for 20 minutes. The silica gel obtained was heated in an oven at $60^{o}C$ for six hours to achieve an activity of III (15% water) on the Brockmann activity scale.

The dark brown liquid was purified by column chromatography over silica gel of activity III, eluting with hexane, and the earliest eluting yellow fraction was collected, leaving a dark brown solid precipitated above the silica gel. The yellow liquid obtained was concentrated by rotovapping and cooled in the refrigerator to induce crystallization. The orange crystals obtained were isolated by decanting, and the filtrate was concentrated by rotovapping and recooled to obtain more solid. The product was characterized by NMR spectroscopy.


CH3
CH3
+ Br2
CCl4
Br
CH3
CH3

Part Five: The Preparation of 3,6-dimethyl-9,10-phenanthrenequinone[3]

A mass of 4.43 g (0.0155 mol) of 9-bromo-3,6-dimethylphenanthrene was dissolved in 118 ml of acetic acid in an Erlenmeyer flask to yield a yellow solution. A solution of 6.2 g (0.062 mol) of chromic trioxide in 88 ml of acetic acid and 44 ml of water was added to the yellow solution to yield a dark brownish-black reaction mixture, which was allowed to stand at ambient temperature in the hood for 15 minutes. The reaction mixture was quenched by pouring it into an equal volume of water to yield a yellow-orange, less dense solid. The solid was dissolved in toluene, and the toluene solution was separated from any contaminating reaction mixture in a separatory funnel. The toluene solution was purified by column chromatography over silica gel, eluting with toluene. The earliest eluting yellowish-orange fraction was collected and rotovapped to dryness to yield a reddish-orange solid. The orange solid was dissolved in hot methylene chloride and cooled in the refrigerator to induce crystallization. The yellowish-orange crystals obtained were isolated by vacuum filtration on a Buchner funnel and washed with a cold hexane-methylene chloride mixture. The filtrate was concentrated by rotovapping and recooled to obtain more solid. The product was characterized by melting point analysis, and IR and NMR spectroscopy.


Br
CH3
CH3
+ CrO3
CH3COOH
H2O
O
O
CH3
CH3
+ Br2

PartSix:The Preparation of 3,6-dimethyl-9,10-bis(trimethylsilyl)diimine[4]

A three-necked, 100 ml, round-bottomed flask was equipped with a thermometer, a magnetic stirring bar, a 125 ml vented addition funnel with a septum, and a nitrogen inlet. A mass of 2.17 g (0.00918 mol) of 3,6-dimethyl-9,10-phenanthrenequinone was added to the reaction flask.

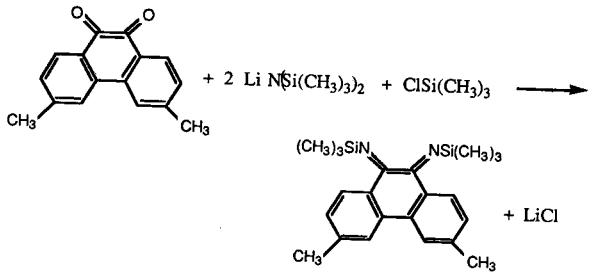
A one-necked, 500 ml, round-bottomed flask was equipped with a thermometer, a condensor, and a 250 ml round-bottomed flask with a side arm. A volume of 250 ml of benzene was dried over molecular sieves in an Erlenmeyer flask. The dried benzene was decanted into the 500 ml round-bottomed flask through a funnel. The benzene was refluxed over sodium and benzophenone until a dark, bluish-green color was achieved. The benzene was distilled under a slow, continuous nitrogen flush.

A volume of 15 ml of the distilled benzene was added to the reaction flask through a syringe through the addition funnel to yield a yellowish-orange mixture. The magnetic stirring apparatus was turned on. A volume of 30 ml of the distilled benzene and 22 ml (0.0220 mol) of lithium-bis-trimethylsilylamide in hexanes were added to the addition funnel through a syringe. The contents of the addition funnel were allowed to drip slowly into the reaction flask to yield an olive green mixture that darkened to greenish-black. The reaction mixture turned dark red after stirring at $70^{o}C$ for 24 hours.

The reaction mixture was allowed to cool to ambient temperature. A volume of 2.8 ml (0.0220 mol) of chlorotrimethylsilane was added to the addition funnel through a syringe and were allowed to drip into the

reaction mixture. The reaction mixture was heated at 60°C for six hours and allowed to cool to ambient temperature, yielding a white precipitate.

The reaction mixture was filtered on a frit under an argon flush and the white solid was discarded. The filtrate was evaporated to yield a dark brownish-green bubbly oil. The oil was dissolved in toluene, and the resulting mixture was filtered on a frit. The solution was concentrated, and the product was crystallized from a toluene/hexane solvent mixture.



Results and Discussion:

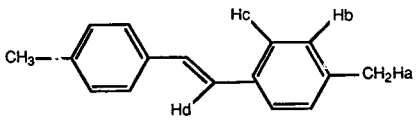
Part One: The Preparation of di-p-tolylchloroethane

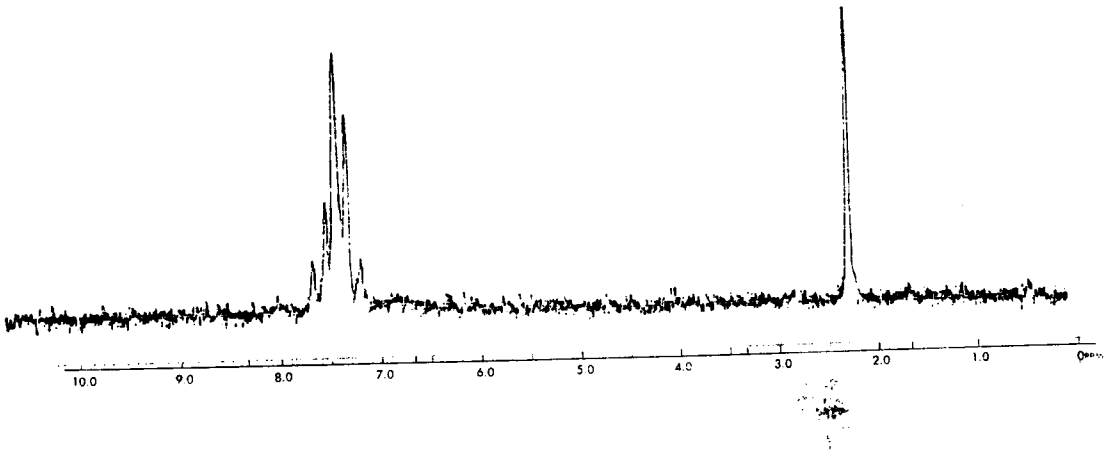
Di-p-tolylchloroethane was synthesized via an α-metallation reaction from α-chloroparaxylene and n-butyllithium according to the procedure outlined in [1]. The reaction apparatus was flame dried and the reaction was carried out under a nitrogen atmosphere to eliminate water, which undergoes an undesirable reaction with the alkyl lithium reagant. The alkyl lithium reagant was added to the reaction mixture slowly in order to prevent a rapid increase in reaction temperature. In contrast to the literature observation, as the alkyl lithium reagant was added, the reaction mixture proceeded through a color change, not to pale orange and then to colorless, but from pale yellow to pale green and back to pale yellow. No observable change occurred as the reaction mixture was allowed to warm to ambient temperature with the slush bath in place. The reaction was allowed to proceed overnight to compensate for the increased scale. Quenching the reaction mixture in ice water yielded a dense, colorless water layer and a less dense, colorless organic layer. Separation, drying, and concentration yielded a clear, yellow oil that was crystallized and filtered to yield the desired product in the form of a white granular solid.

Part Two: The Preparation of 4,4'-dimethyl-trans-stilbene

4,4'-dimethyl-trans-stilbene was synthesized via a dehydrohalogenation reaction from di-p-tolylchloroethane according to a modified version of the procedure outlined in [1]. Due to the larger scale of the reaction, the microdistillation assembly was replaced by a three-necked, 500 ml, round-bottomed flask with a condenser and bubbler. A heating mantle was used in place of a microburner to achieve more uniform and continuous heating, which resulted in a slow rather than an instantaneous evolution of hydrogen chloride. The reaction was carried out under a nitrogen flow to eliminate first the vapors of the diethyl ether solvent, which had been used to facilitate reactant transfer, and then the hydrogen chloride vapors that were evolved as the reaction proceeded, thereby driving the equilibrium to favor the desired product. As the reaction proceeded, the reaction mixture underwent a color change from colorless to brown that was not cited in the literature. The product white solid was recrystallized from absolute ethanol rather than from a larger volume tetrahydrofuran-petroleum ether solvent system. The desired product was obtained in the form of crystalline white needles rather than platelets. The product was characterized by NMR spectroscopy (see figure 1) utilizing deuterobenzene as the solvent. The following peaks were observed, and were assigned, respectively, to Ha,Hd,Hb,and Hc, and benzene.

peak	ppm
singlet	2.23
singlet	6.92
doublet of doublets	6.92, 7.04, 7.25, 7.40
singlet	7.15




10.0
9.0
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4.0
3.0
2.0
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0 ppm

Correction

of

PRECEDING DOCUMENT

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P.O. Box 640, Port Ewen, New York 12466
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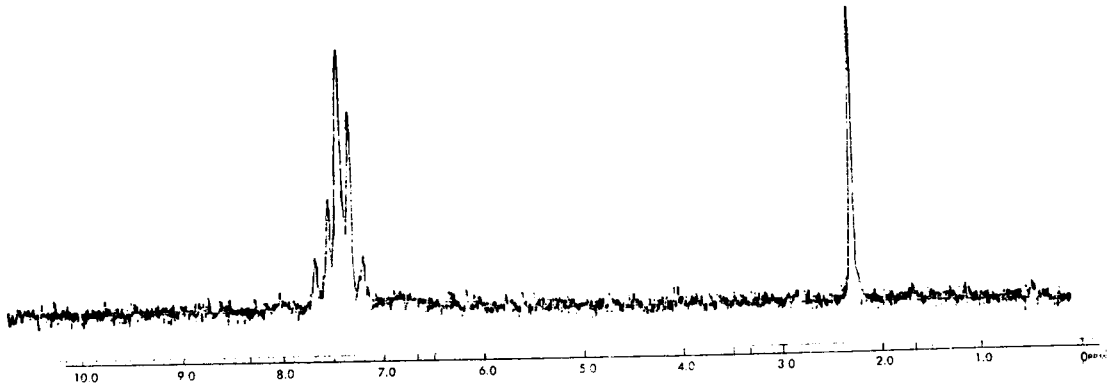
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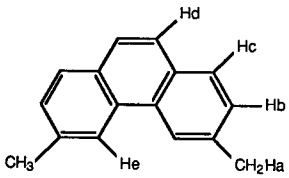
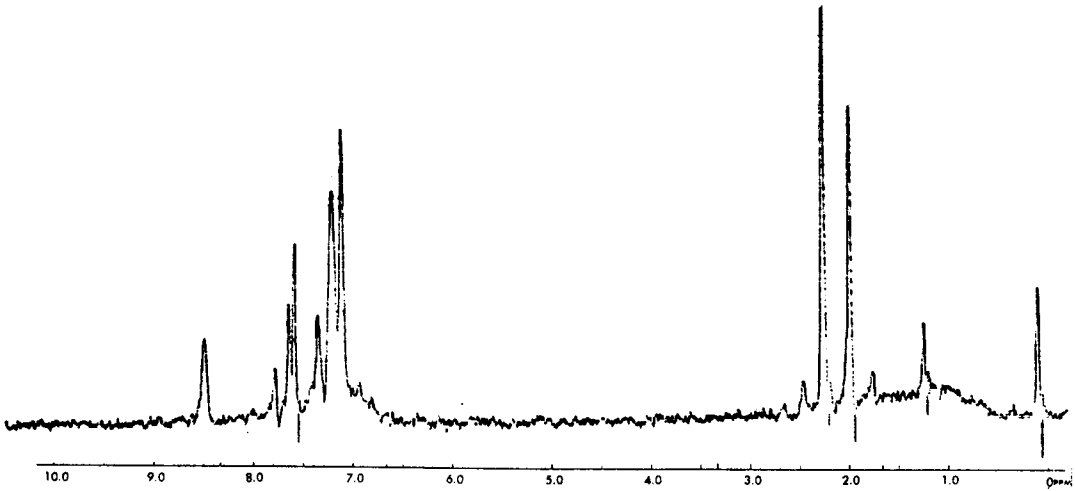
Part Three: The Preparation of 3,6-dimethylphenanthrene

3,6-dimethylphenanthrene was synthesized via a photocyclization reaction from 4,4'-dimethyl-trans-stilbene according to a modified version of the procedure outlined in [2]. Instead of carrying out the reaction in an Erlenmeyer flask, the reaction was carried out in a commercially available photolysis apparatus. The water bath was replaced by a water jacket in the photolysis apparatus, and air was bubbled through the reaction mixture at a steady flow rate. In addition, a condenser was added to the photolysis apparatus to prevent loss of solvent. Cyclohexane was utilized as the solvent rather than a 5:1 cyclohexane/benzene solvent mixture in an effort to prevent solvent absorption of the radiation. In addition, a mercury Hanovia lamp was utilized rather than the weaker mercury lamp that was used in the literature procedure. These modifications reduced the necessary irradiation time from 18.5 hours to 2 hours. The end of the reaction was characterized by the appearance of a white precipitate on the walls of the reaction vessel and a color change of the reaction mixture from violet to orange. Evaporation of the reaction mixture and recrystallization of the resulting orange solid from methanol yielded the desired product in the form of crystalline orangish-gold needles. The product was characterized by NMR spectroscopy, utilizing deuterobenzene as the solvent (see figure 2). The following peaks were observed, and were assigned, respectively, to cyclohexane, Ha , benzene, Hb and Hc , and He .

peak	ppm
singlet	1.40
singlet	2.36
singlet	7.41
double [illegible] doublets	7.46, 7.48, 7.65
singlet	8.33

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6.0
5.0
4.0
3.0
2.0
1.0
0PPM

Part Four: The Preparation of 9-bromo-3,6-dimethylphenanthrene

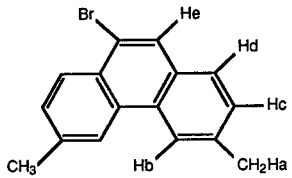
9-bromo-3,6-dimethylphenanthrene was synthesized in 67.4% yield via a dibromination reaction, followed by a dehydrobromination reaction according to the procedure outlined in [3]. Addition of the bromine to the reaction mixture yielded a reddish-brown solution, which underwent no observable change over the course of the dibromination reaction. Rotary evaporation of the carbon tetrachloride solvent yielded a dark brown oil, which yielded an oily brown solid upon standing overnight.

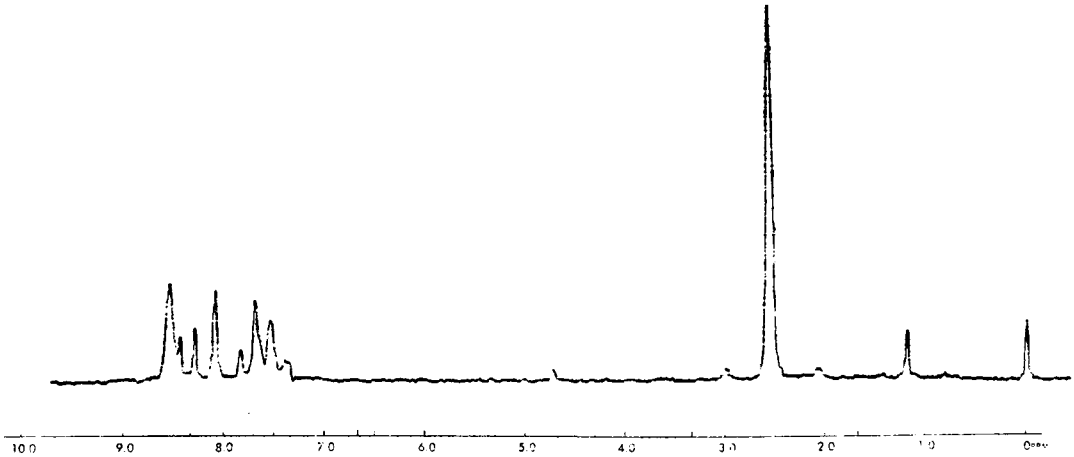
The dehydrobromination reaction was carried out by heating the oil and solid over a steam bath for 30 minutes. The resulting dark brown oil was purified by column chromatography over silica gel, eluting with hexanes. A dark brown solid and yellow liquid were observed. The yellow liquid was concentrated and allowed to crystallize to yield the desired product in the form of orange crystals.

The product was characterized by NMR spectroscopy (see figure 3) utilizing deutero-chloroform as the solvent. The following peaks were observed, and were assigned, respectively to Ha, Hc and Hf,He, Hd, and Hb .

peak	ppm
singlet	2.6
doublet of doublets	7.2, 7.4, 7.52, 7.68

peak	ppm
singlet	7.91
doublet	8.1, 8.25
singlet	8.35

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9.0
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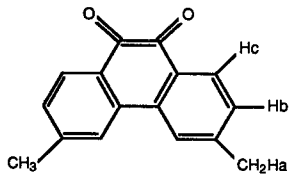
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0ppm

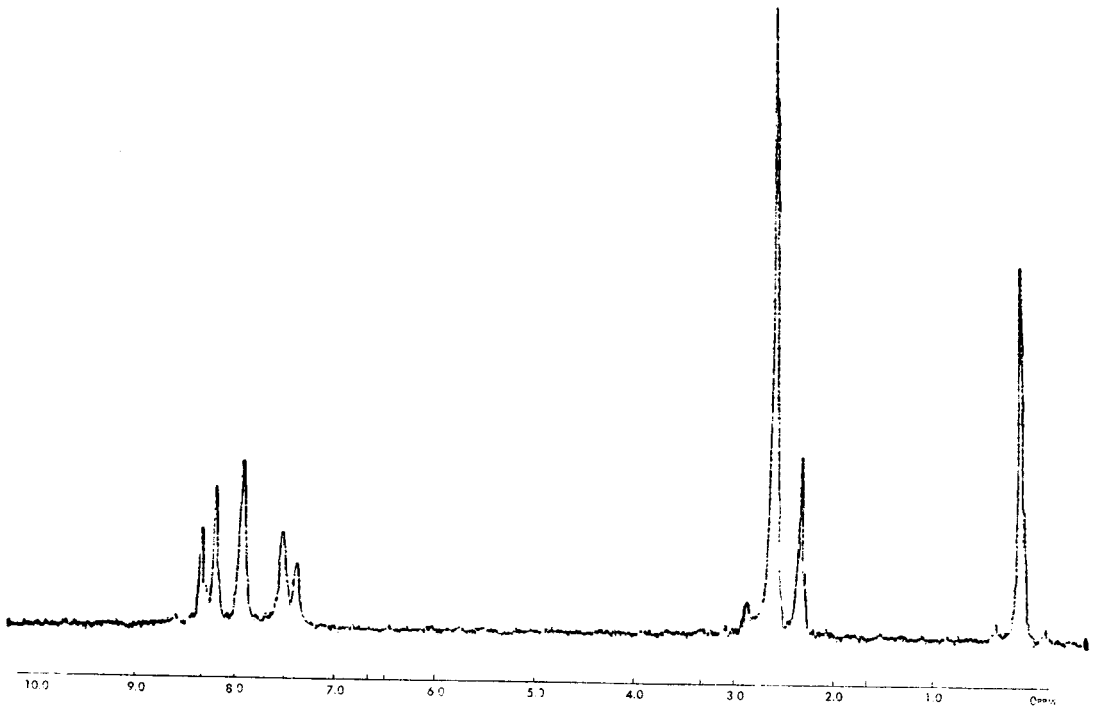
Part Five: The Preparation of 3,6-dimethyl-9,10-phenanthrenequinone

3,6-dimethyl-9,10-phenanthrenequinone was synthesized in 59.2% yield via an oxidation reaction from 9-bromo-3, dimethylphenanthrene according to the procedure outlined in [3]. When the dark reddish-orange chromium trioxide solution was mixed with the yellow reactant solution, the reaction mixture underwent a color change to dark brownish-black. Quenching the reaction mixture in water yielded a yellowish-orange solid floating at the top of the dark brownish-black solution. In clarification of the literature procedure, this solid was isolated by dissolving it in toluene and separating the solution from the reaction mixture. The solid was then purified by column chromatography on silica gel, eluting, in clarification of the literature procedure, with toluene. A yellow solid and a yellowish-orange liquid were observed. The yellowish-orange liquid was concentrated to yield an orange solid. As an addition to the literature procedure, the orange solid was then recrystallized from methylene chloride to yield the desired product in the form of crystalline yellowish-orange needles. The product was characterized by melting point, NMR spectroscopy (see figure 4) and IR spectroscopy (see figure 5).

The product melted over the temperature range of 217-221^{o}C. Utilizing chloroform as the solvent and reference material, the starred peaks were observed in the IR spectrum. Utilizing deuterochloroform as the solvent, the following peaks were observed in the NMR spectrum, and were assigned, respectively to Ha, Hb, Hd, and Hc .

peak	ppm
singlet	2.33
doublet	6.89, 7.02
singlet	7.41
doublet	7.68, 7.80

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9.0
8.0
7.0
6.0
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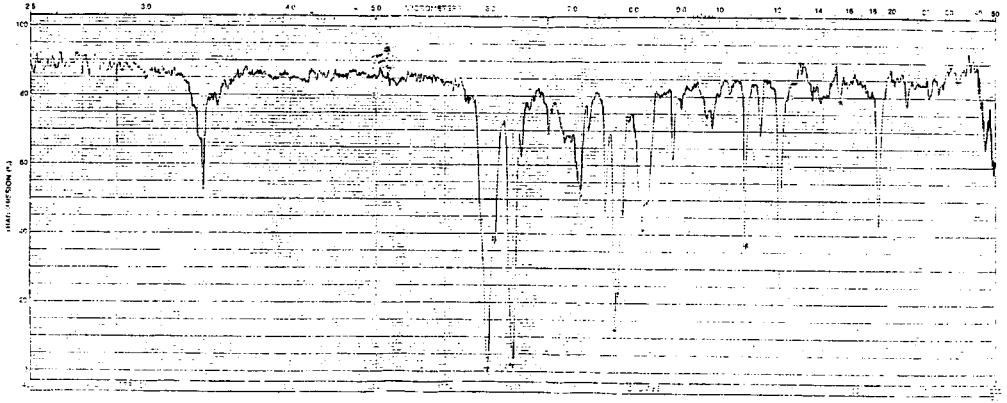
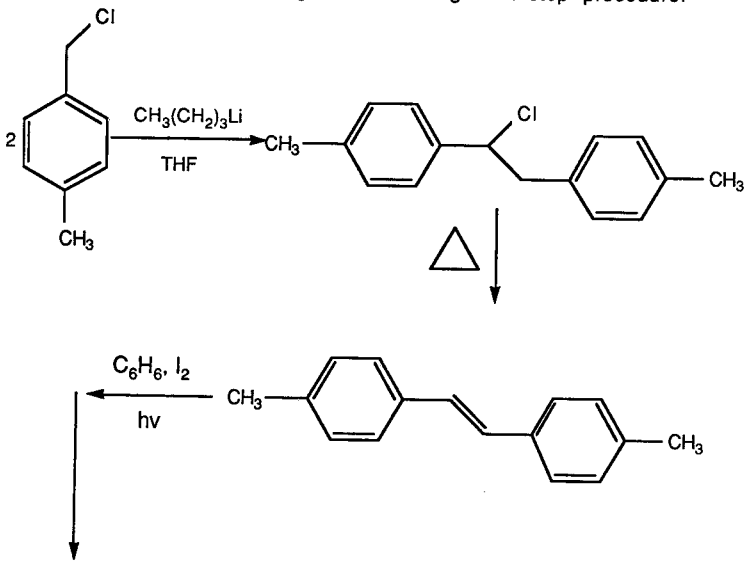


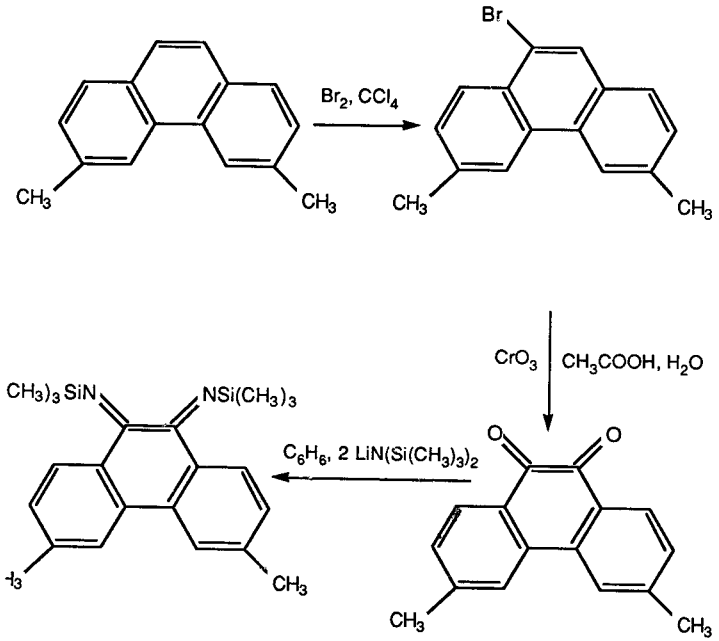
Part Six: The Preparation of 3,6-dimethyl-9,10-bis(trimethylsilyl)diimine

3,6-dimethyl-9,10-bis(trimethylsilyl)diimine was synthesized from 3,6-dimethyl-9,10-phenanthrenequinone according to the procedure outlined in [4], with one modification. Lithium trimethylsilylamide was used in place of its sodium analog. The benzene solvent was dried and distilled , and the reaction was carried out under a nitrogen atmosphere to eliminate water, since water undergoes an undesirable reaction with the lithium reagant. The addition of the chlorotrimethylsilane reagant to the reaction mixture resulted in the precipitation of solid white lithium chloride. Filtration and evaporation yielded the desired product the form of a dark brownish-green oil. As a modification to the literature procedure, the product was purified by dissolving in toluene, filtering, concentrating, and crystallizing from a toluene/hexane solvent mixture. The desired product is extremely air and water sensitive, and undergoes a color change to green immediately upon exposure to air.

Conclusion:

The 3,6-dimethyl analog of donor molecule precursor (I) was sucessfully synthesized through the following multi-step procedure.





Preliminary investigations of the product indicate improved solubility in non-aromatic solvents compared to compound (I), thus enhancing its potential usefulness as a donor molecule precursor.

Endnotes

[1] D.F. Hoeg and D.I. Lusk,"Halo-Carbanion Intermediates: Synthesis of α-Chlorobenzyls and Stilbenes via the α-metallation of benzylchlorides with n-Butyllithium", Journal of Organometallic Chemistry, Volume 5, 1966, pages 1-12

[2] H.A. Staub,U.E. Meissner,and B. Meissner,"Phenanthro[cdefg][18]annulen und Dibenzo[ab,de][18]annulen", Chem. Ber., Volume 109, 1976, pages 3875-3885

[3] M.S. Newman and K.C. Lilje, "Synthesis of 9-Bromoderivatives of 4,5-, 2,7-, and 3,6-, Dimethyl- and 2,4,5,7-, and 3,4,5,6- Tetramethyl-phenanthrenes", Journal of Organic Chemistry, Volume 44, No. 26, 1979, pages 4944-4946

[4] G. Tuchtenhagen and K. Ruhlmann, "Darstellung und Reaktionen von 1.2-Bis-trimethylsilyliminen", Liebigs Ann. Chem., Volume 711, 1968, pages 174-183

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